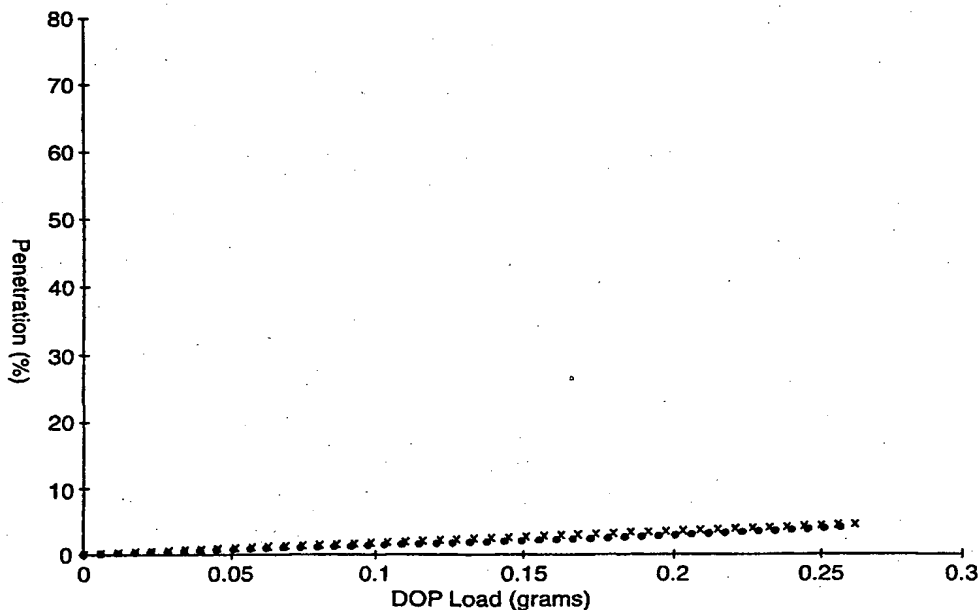




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(5i) International Patent Classification <sup>7</sup> : C08F 8/24, B03C 3 /28		A1	(11) International Publication Number: <b>WO 00/01737</b>
			(43) International Publication Date: 13 January 2000 (13.01.00)
(21) International Application Number: PCT/US99/13917		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: 21 June 1999 (21.06.99)			
(30) Priority Data: 09/109,497 2 July 1998 (02.07.98) US			
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(54) Title: FLUORINATED ELECTRET



## (57) Abstract

An electret that includes a surface modified polymeric article having surface fluorination produced by fluorinating the polymeric article. The electret may be a nonwoven fibrous web that comprises electrically charged microfibers where the web has fluorination that includes CF<sub>3</sub> and CF<sub>2</sub> groups on the surface of the fibers at a CF<sub>3</sub>:CF<sub>2</sub> ratio of at least 0.45.

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## FLUORINATED ELECTRET

This invention relates to preparing fluorinated electrets.

5

### BACKGROUND

The filtration properties of nonwoven polymeric fibrous webs can be improved by transforming the web into an electret, i.e., a dielectric material exhibiting a quasi-permanent electrical charge. Electrets are effective in enhancing particle capture in aerosol filters. Electrets are useful in a variety of devices including, e.g., air filters, face masks, and respirators, and as electrostatic elements in electro-acoustic devices such as microphones, headphones, and electrostatic recorders.

Electrets are currently produced by a variety of methods including direct current ("DC") corona charging (see, e.g., U.S. Patent 30,782 (van Turnhout)), and hydrocharging (see, e.g., U.S. Patent 5,496,507 (Angadjivand et al.)), and can be improved by incorporating fluorochemicals into the melt used to produce the fibers of some electrets (see, e.g., U.S. Patent 5,025,052 (Crater et al.)).

Many of the particles and contaminants with which electret filters come into contact interfere with the filtering capabilities of the webs. Liquid aerosols, for example, particularly oily aerosols, tend to cause electret filters to lose their electret enhanced filtering efficiency (see, e.g., U.S. Patent 5,411,576 (Jones et al.)).

Numerous methods have been developed to compensate for loss of filtering efficiency. One method includes increasing the amount of the nonwoven polymeric web in the electret filter by adding layers of web or increasing the thickness of the electret filter. The additional web, however, increases the breathing resistance of the electret filter, adds weight and bulk to the electret filter, and increases the cost of the electret filter. Another method for improving an electret filter's resistance to oily aerosols includes forming the electret filter from resins that include melt processable fluorochemical additives such as fluorochemical oxazolidinones, fluorochemical piperazines, and perfluorinated alkanes. (See, e.g., U.S. Patent 5,025,052 (Crater et al.)). The fluorochemicals should be melt processable, i.e., suffer substantially no degradation under the melt processing conditions used to form the microfibers that are used in the fibrous webs of some electrets. (See, e.g., WO 97/07272 (Minnesota Mining and Manufacturing)).

SUMMARY OF THE INVENTION

In one aspect, the invention features an electret that includes a surface modified polymeric article having surface fluorination produced by fluorinating a polymeric article.

5 In one embodiment, the article includes at least about 45 atomic % fluorine as detected by ESCA. In another embodiment, the article includes a  $\text{CF}_3:\text{CF}_2$  ratio of at least about 0.25 as determined according to the Method for Determining  $\text{CF}_3:\text{CF}_2$ . In other embodiments, the article includes a  $\text{CF}_3:\text{CF}_2$  ratio of at least about 0.45 as determined according to the Method for Determining  $\text{CF}_3:\text{CF}_2$ .

10 In one embodiment, the article has a Quality Factor of at least about 0.25/mmH<sub>2</sub>O, (preferably at least about 0.5/mmH<sub>2</sub>O, more preferably at least about 1/mmH<sub>2</sub>O).

In some embodiments, the article includes a nonwoven polymeric fibrous web. Examples of suitable fibers for the nonwoven polymeric fibrous web include  
15 polycarbonate, polyolefin, polyester, halogenated polyvinyl, polystyrene, and combinations thereof. Particularly useful fibers include polypropylene, poly-(4-methyl-1-pentene), and combinations thereof. In one embodiment, the article includes meltblown microfibers.

In another aspect, the invention features an electret that includes a polymeric  
20 article having at least about 45 atomic % fluorine as detected by ESCA, and a  $\text{CF}_3:\text{CF}_2$  ratio of at least about 0.45 as determined according to the Method for Determining  $\text{CF}_3:\text{CF}_2$ . In another embodiment, the electret includes at least about 50 atomic % fluorine as detected by ESCA, and a  $\text{CF}_3:\text{CF}_2$  ratio of at least about 0.25 as determined according to the Method for Determining  $\text{CF}_3:\text{CF}_2$ .

25 In other aspects, the invention features a respirator that includes the above-described electrets. In still other aspects, the invention features a filter that includes the above-described electrets.

In one aspect, the invention features a method of making an electret that includes: (a) fluorinating a polymeric article to produce an article having surface  
30 fluorination; and (b) charging the fluorinated article in a manner sufficient to produce an electret. In one embodiment, the method includes charging the fluorinated article by contacting the fluorinated article with water in a manner sufficient to produce an electret,

and drying the article. The method is useful for making the above-described electrets. In another embodiment, the method includes charging the fluorinated article by impinging jets of water or a stream of water droplets onto the fluorinated article at a pressure and for a period sufficient to produce an electret, and drying the article.

5 In other embodiments, the method includes fluorinating a polymeric article in the presence of an electrical discharge (e.g., an alternating current corona discharge at atmospheric pressure) to produce a fluorinated article. In one embodiment, the method includes fluorinating the polymeric article in an atmosphere that includes fluorine containing species selected from the group consisting of elemental fluorine, fluorocarbons, 10 hydrofluorocarbons, fluorinated sulfur, fluorinated nitrogen and combinations thereof. Examples of suitable fluorine containing species include  $C_3F_{12}$ ,  $C_2F_6$ ,  $CF_4$ , hexafluoropropylene,  $SF_6$ ,  $NF_3$ , and combinations thereof.

In other embodiments, the method includes fluorinating the polymeric article in an atmosphere that includes elemental fluorine.

15 In other embodiments, the method of making the electret includes: (A) fluorinating a nonwoven polymeric fibrous web (i) in an atmosphere that includes fluorine containing species and an inert gas, and (ii) in the presence of an electrical discharge to produce a web having surface fluorination; and (B) charging the fluorinated web in a manner sufficient to produce an electret.

20 In other aspects, the invention features a method of filtering that includes passing an aerosol through the above-described electrets to remove contaminants.

The fluorinated electrets of the invention exhibit a relatively high oily mist resistance relative to non-fluorinated electrets.

## 25 GLOSSARY

In reference to the invention, these terms having the meanings set forth below:

"electret" means a dielectric material exhibiting a quasi-permanent electrical charge. The term "quasi-permanent" means that the time constants characteristic for the decay of the charge are much longer than the time period over which the electret is used;

30 "surface modified" means that the chemical structure at the surface has been altered from its original state.

"surface fluorination" means the presence of fluorine atoms on a surface (e.g., the surface of an article);

"fluorine containing species" means molecules and moieties containing fluorine atoms including, e.g., fluorine atoms, elemental fluorine, and fluorine containing radicals;

5 "fluorinating" means placing fluorine atoms on the surface of an article by transferring fluorine containing species from a gaseous phase to the article by chemical reaction, sorption, condensation, or other suitable means;

"aerosol" means a gas that contains suspended particles in solid or liquid form; and

10 "contaminants" means particles and/or other substances that generally may not be considered to be particles (e.g., organic vapors).

#### BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a plot of % DOP Penetration vs. DOP Load for Examples 36 and 37.

15 Fig. 2 is a plot of % DOP Penetration vs. DOP Load for Examples 38 and 39.

Fig. 3 is a plot of % DOP Penetration vs. DOP Load for Example 40.

#### DESCRIPTION OF PREFERRED EMBODIMENTS

The electret includes a surface modified polymeric article (e.g., a nonwoven  
20 polymeric fibrous web) produced by fluorinating a polymeric article. The electrets preferably have sufficient surface fluorination to provide oily mist resistance. One measure of oily mist resistance is how well the electret maintains its Quality Factor during challenge with an aerosol. The Quality Factor can be calculated from results obtained from the dioctylphthalate ("DOP") initial penetration test ("the DOP test"). The DOP test  
25 also provides a relative measure of the charge state of the filter. The DOP test procedure involves forcing DOP aerosol at a face velocity of 6.9 cm/second for a period of about 30 seconds through the sample, measuring the pressure drop across the sample (Pressure Drop measured in mmH<sub>2</sub>O) with a differential manometer, and measuring the percent DOP penetration (DOPPen %). The Quality Factor (QF) (measured in 1/mmH<sub>2</sub>O) can be  
30 calculated from these values according to the following formula:

$$QF[1/mm\ H_2O] = \frac{-\ln \frac{DOP\ Penetration(\%)}{100}}{Pressure\ Drop[mm\ H_2O]}$$

The higher the Quality Factor at a given flow rate, the better the filtering performance of the electret.

Preferred electrets have a Quality Factor of at least about 0.25/mmH<sub>2</sub>O, preferably at least about 0.5/mmH<sub>2</sub>O, more preferably at least about 1.0/mmH<sub>2</sub>O.

Electron spectroscopy for chemical analysis ("ESCA") (also known as X-ray photoelectron spectroscopy ("XPS")) provides one measure of surface fluorination. Preferably the surface of the electret exhibits at least about 45 atomic % fluorine, more preferably at least about 50 atomic % fluorine when analyzed by ESCA. ESCA analyzes the elemental composition of the outermost surface (i.e., approximately 10 to 50 Å) of a specimen. ESCA can be used to detect all elements in the periodic table except helium and hydrogen.

The electret also has a CF<sub>3</sub>:CF<sub>2</sub> ratio at the surface of the electret of at least about 0.25, preferably at least about 0.45, and more preferably greater than 0.9, as determined according to the Method For Determining CF<sub>3</sub>:CF<sub>2</sub> ratio set forth in the Example section below.

In one embodiment, the electrets include nonwoven polymeric fibrous webs that include fibers such as, e.g., meltblown microfibers, staple fibers, fibrillated films, and combinations thereof. The fibers can be formed from resins. Preferably the resin is a thermoplastic nonconductive, i.e., having a resistivity of greater than 10<sup>14</sup> ohm-cm, resin. The resin used to form the fibers should be substantially free of materials such as antistatic agents that could increase the electrical conductivity or otherwise interfere with the ability of the fibers to accept and hold electrostatic charges.

Examples of useful thermoplastic resins include polyolefins such as, e.g., polypropylene, polyethylene, poly-(4-methyl-1-pentene), and combinations thereof, halogenated vinyl polymers (e.g., polyvinyl chloride), polystyrene, polycarbonates, polyesters, and combinations thereof.

Additives can be blended with the resin including, e.g., pigment, UV stabilizers, antioxidants, and combinations thereof.

The electret may comprise a nonwoven web that contains polymeric fibers, including microfibers such as meltblown microfibers. Meltblown microfibers can be prepared as described in Wentz, Van A., "Superfine Thermoplastic Fibers," Industrial Eng. Chemistry, Vol. 48, pp. 1342-1346 and in Report No. 4364 of the Naval Research laboratories, published May 25, 1954, entitled, "Manufacture of Super Fine Organic Fibers, " by Wentz et al. Meltblown microfibers preferably have an effective fiber diameter in the range of less than 1 to 50 micrometers ( $\mu\text{m}$ ) as calculated according to the method set forth in Davies, C.N., "The Separation of Airborne Dust and Particles," Institution of Mechanical Engineers, London, Proceedings 1B, 1952. Blown microfibers for fibrous electret filters typically have an effective fiber diameter from about 3 to 30 micrometers, preferably from about 7 to 15 micrometers.

The presence of staple fibers provides a more lofty, less dense web than a web constructed solely of meltblown microfibers. Preferably the electret contains more than 70% by weight staple fibers. Webs containing staple fibers are disclosed in U.S. Patent No. 4,118,531 (Hauser).

Electrets that include a nonwoven polymeric fibrous web preferably have a basis weight in the range of about 10 to 500  $\text{g/m}^2$ , more preferably about 10 to 100  $\text{g/m}^2$ . The thickness of the nonwoven polymeric fibrous web is preferably about 0.25 to 20 mm, more preferably about 0.5 to 2 mm.

The nonwoven polymeric webs of the electret can also include particulate matter as disclosed, for example, in U.S. Patent Nos. 3,971,373, (Braun), 4,100,324 (Anderson), and 4,429,001 (Kolpin et al.).

#### Electret Preparation

The electrets can be prepared by fluorinating a polymeric article, optionally in the presence of a surface modifying electrical discharge, and charging the fluorinated article to produce an electret.

The fluorination process includes modifying the surface of the polymeric article to contain fluorine atoms by exposing the polymeric article to an atmosphere that includes fluorine containing species. The fluorination process can be performed at



atmospheric pressure or under reduced pressure. The fluorination process is preferably performed in a controlled atmosphere to prevent contaminants from interfering with the addition of fluorine atoms to the surface of the article. The atmosphere should be substantially free of oxygen and other contaminants. Preferably the atmosphere contains  
5 less than 0.1 % oxygen.

The fluorine containing species present in the atmosphere can be derived from fluorinated compounds that are gases at room temperature, become gases when heated, or are capable of being vaporized. Examples of useful sources of fluorine containing species include, fluorine atoms, elemental fluorine, fluorocarbons (e.g.,  $C_3F_{12}$ ,  $C_2F_6$ ,  $CF_4$ , and  
10 hexafluoropropylene), hydrofluorocarbons (e.g.,  $CF_3H$ ), fluorinated sulfur (e.g.,  $SF_6$ ), fluorinated nitrogen (e.g.,  $NF_3$ ), fluorochemicals such as e.g.,  $CF_3OCF_3$  and fluorochemicals available under the trade designation Fluorinert such as, e.g., Fluorinert FC-43 (commercially available from Minnesota Mining and Manufacturing Company, Minnesota), and combinations thereof.

15 The atmosphere of fluorine containing species can also include an inert diluent gas such as, e.g., helium, argon, nitrogen, and combinations thereof.

The electrical discharge applied during the fluorination process is capable of modifying the surface chemistry of the polymeric article when applied in the presence of a source of fluorine containing species. The electrical discharge is in the form of plasma,  
20 e.g., glow discharge plasma, corona plasma, silent discharge plasma (also referred to as dielectric barrier discharge plasma and alternating current ("AC") corona discharge), and hybrid plasma, e.g., glow discharge plasma at atmospheric pressure, and pseudo glow discharge. Preferably the plasma is an AC corona discharge plasma at atmospheric pressure. Examples of useful surface modifying electrical discharge processes are  
25 described in U.S. Patent 5,244,780, U.S. Patent 4,828,871, and U.S. Patent No. 4,844,979.

Another fluorination process includes immersing a polymeric article into a liquid that is inert with respect to elemental fluorine, and bubbling elemental fluorine gas through the liquid to produce a surface fluorinated article. Examples of useful liquids that are inert with respect to fluorine include perhalogenated liquids, e.g., perfluorinated  
30 liquids such as Performance Fluid PF 5052 (commercially available from Minnesota Mining and Manufacturing Company). The elemental fluorine containing gas that is

bubbled through the liquid can include an inert gas such as, e.g., nitrogen, argon, helium, and combinations thereof.

Charging the polymeric article to produce an electret can be accomplished using a variety of techniques, including, e.g., hydrocharging, i.e., contacting an article with water in a manner sufficient to impart a charge to the article, followed by drying the article, and DC corona charging. The charging process can be applied to one or more surfaces of the article.

One example of a useful hydrocharging process includes impinging jets of water or a stream of water droplets onto the article at a pressure and for a period sufficient to impart a filtration enhancing electret charge to the web, and then drying the article. The pressure necessary to optimize the filtration enhancing electret charge imparted to the article will vary depending on the type of sprayer used, the type of polymer from which the article is formed, the type and concentration of additives to the polymer, and the thickness and density of the article. Pressures in the range of about 10 to about 500 psi (69 to 3450 kPa) are suitable. An example of a suitable method of hydrocharging is described in U.S. Patent No. 5,496,507 (Angadjivand et al.).

The jets of water or stream of water droplets can be provided by any suitable spray device. One example of a useful spray device is the apparatus used for hydraulically entangling fibers.

Examples of suitable DC corona discharge processes are described in U.S. Patent 30,782 (van Turnhout), U.S. Patent 31,285 (van Turnhout), U.S. Patent 32,171 (van Turnhout), U.S. Patent 4,375,718 (Wadsworth et al.), U.S. Patent 5,401,446 (Wadsworth et al.), U.S. Patent 4,588,537 (Klasse et al.), and 4,592,815 (Nakao).

The fluorinated electrets formed by the methods described herein are suitable for use as, e.g., electrostatic elements in electro-acoustic devices such as microphones, headphones and speakers, fluid filters, dust particle control devices in, e.g., high voltage electrostatic generators, electrostatic recorders, respirators (e.g., prefilters, canisters and replaceable cartridges), heating, ventilation, air conditioning, and face masks.

The invention will now be described further by way of the following examples.

## EXAMPLES

### Test Procedures

Test procedures used in the examples include the following.

#### 5 Method for Determining CF<sub>3</sub>:CF<sub>2</sub>

ESCA data was collected on a PHI 5100 ESCA system (Physical Electronics, Eden Prairie, Minnesota) using a non-monochromatic MgK $\alpha$  x-ray source and a 45 degree electron takeoff angle with respect to the surface. The carbon (1s) spectra were peak fit using a nonlinear least-squares routine supplied by PHI (Physical Electronics, Eden Prairie, Minnesota). This routine used a linear background subtraction, and a gaussian peak shape for the component peaks. The spectra were referenced to the hydrocarbon peak at 285.0 eV. The CF<sub>3</sub> and CF<sub>2</sub> components were identified as the peaks located at about 294 eV and 292 eV respectively (according to the procedure described in Strobel et al., J. Polymer Sci. A: Polymer Chemistry, Vol. 25, pp. 1295-1307 (1987)). The CF<sub>3</sub>:CF<sub>2</sub> ratio represent the ratio of the peak areas of the CF<sub>3</sub> and CF<sub>2</sub> components.

#### Initial Dioctylphthalate Penetration (DOP) and Pressure Drop Test Procedure

Initial DOP penetration is determined by forcing 0.3 micrometer diameter dioctyl phthalate (DOP) particles at a concentration of between 70 and 140 mg/m<sup>3</sup> (generated using a TSI No. 212 sprayer with four orifices and 30 psi clean air) through a sample of filter media which is 4.5 inches in diameter at a rate of 42.5 L/min (a face velocity of 6.9 centimeters per second). The sample is exposed to the DOP aerosol for 30 seconds until the readings stabilize. The penetration is measured with an optical scattering chamber, Percent Penetration Meter Model TPA-8F available from Air Techniques Inc.

25 Pressure drop across the sample is measured at a flow rate of 42.5 L/min (a face velocity of 6.9 cm/sec) using an electronic manometer. Pressure drop is reported in mm of water ("mm H<sub>2</sub>O").

DOP penetration and pressure drop are used to calculate the quality factor "QF" from the natural log (ln) of the DOP penetration by the following formula:

$$QF[1/mm H_2O] = \frac{-\ln \frac{DOP Penetration(\%)}{100}}{Pressure Drop[mm H_2O]}$$

A higher initial QF indicates better initial filtration performance. A decreased QF effectively correlates with decreased filtration performance.

### DOP Loading Test

5 DOP loading is determined using the same test equipment used in the DOP penetration and pressure drop tests. The test sample is weighed and then exposed to the DOP aerosol for at least 45 min to provide a minimum exposure of at least about 130 mg. DOP penetration and pressure drop are measured throughout the test at least as frequently as once per minute. The mass of DOP collected is calculated for each measurement  
10 interval from the measured penetration, mass of the filter web, and total mass of DOP collected on the filter web during exposure ("DOP Load").

### Corona Fluorination

#### EXAMPLE 1

15 A blown polypropylene microfiber web prepared from Exxon 3505G polypropylene resin (Exxon Corp.) and having an effective fiber diameter of 7.5 micrometers ( $\mu m$ ) and a basis weight of 62 g/m<sup>2</sup> was prepared as described in Wentz, Van A., "Superfine Thermoplastic Fibers," Industrial Eng. Chemistry, Vol. 48, pp. 1342-1346.

The blown microfiber web was then AC corona fluorinated in a 1% by volume C<sub>2</sub>F<sub>6</sub> in helium atmosphere at a corona energy of 34 J/cm<sup>2</sup>, which corresponded to a  
20 corona power of 2000W at a substrate speed of 1 m/min. The AC corona fluorination treatment was performed in an AC corona system that included the so-called "double-dielectric" electrode configuration with a ground roll consisting of 40 cm diameter nickel-plated aluminum roll covered with 1.5 mm of poly(ethylene terephthalate) and maintained  
25 at a temperature of 23 °C using recirculating, pressurized water. The powered electrodes consisted of 15 individual ceramic-covered electrodes (available from Sherman treaters Ltd., Thame, United Kingdom) each with a 15 mm square cross-section and an active length of 35 cm. The electrodes were connected to a model RS48-B (4 kW) variable-

frequency power supply (available from ENI Power Systems Inc., Rochester, NY). The net power dissipated in the AC corona was measured with a directional power meter incorporated into the ENI supply. The frequency of the output power was manually adjusted to about 16 kHz to obtain optimal impedance matching (minimum reflected power).

The AC corona system was enclosed within a controlled environment. Prior to treatment, the atmosphere surrounding the AC corona treatment system was purged with helium, and then continually flushed with 100 liters/min of 1% by volume  $C_2F_6$  in helium, which was introduced near the electrodes.

The microfiber web was taped onto a carrier film of 0.05 mm thick bi-axially-oriented polypropylene (BOPP), and then placed on the ground roll such that the carrier film was in contact with the ground roll, causing one side of the blown microfiber web to be exposed to the discharge. After treatment, the blown microfiber web was flipped over, retaped to the carrier film, and AC corona treated a second time under the same conditions as the first treatment to expose the other side of the blown microfiber web to the discharge.

#### EXAMPLE 2

A G100 Filtrete fibrillated film web (available from Minnesota Mining and Manufacturing), having a basis weight of  $100 \text{ g/m}^2$ , was corona fluorinated following the method described in Example 1, with the exception that the ground roll was maintained at a temperature of  $25^\circ\text{C}$ .

#### EXAMPLE 3

A polyethylene meltblown microfiber web, prepared from Aspun PE-6806 polyethylene resin (DOW Chemical Company, Michigan) and having a basis weight of  $107 \text{ g/m}^2$ , was corona fluorinated following the method described in Example 2.

#### EXAMPLE 4

A polyester staple fiber web (available from Rogers Corporation), having a basis weight of  $200 \text{ g/m}^2$ , was corona fluorinated following the method described in Example 2.

**EXAMPLE 5**

A poly-4-methyl-1-pentene meltblown microfiber web prepared from TPX MX-007 poly-4-methyl-1-pentene resin (Mitsui), and having a basis weight of 50 g/m<sup>2</sup> and an effective fiber diameter of 8.1  $\mu$ m, was corona fluorinated following the method described in Example 2.

**EXAMPLES 6-9**

Examples 6-9 were prepared following the procedure in Example 1 except that the source of fluorine containing species was as follows: 1% CF<sub>4</sub> (Example 6), and 0.1% hexafluoropropylene (Example 7), 0.1% C<sub>5</sub>F<sub>12</sub> (Example 8), and 1.0% C<sub>5</sub>F<sub>12</sub> (Example 9).

The surface chemistry of each of the sample webs of Examples 1-9 was determined by ESCA analysis using a PHI 5100 ESCA system. The CF<sub>3</sub>:CF<sub>2</sub> ratio was determined for each of the samples of Examples 1-9 from the ESCA data according to the above-described method. The results are reported in atomic % in Table I.

**TABLE I**

Example	Carbon	Nitrogen	Oxygen	Fluorine	CF <sub>3</sub> :CF <sub>2</sub>
1	43		5.7	51	1.09
2	44		6.2	50	1.37
3	49	0.2	8.2	42	1.10
4	42	0.5	7.8	49	0.99
5	44	0.0	2.9	53	1.19
6	41		3.5	55	0.86
7	41		2.7	56	0.97
8	42		6.4	52	0.91
9	43		5.2	51	0.89

Hydrocharging

## EXAMPLE 10

A fluorinated polypropylene blown microfiber web prepared as described above in Example 1, was passed over a vacuum slot at a rate of 5 cm/sec (centimeters/second) while deionized water was sprayed onto the web at a hydrostatic pressure of about 90 psi from a pair of Spraying Systems Teejet 9501 sprayer nozzles mounted 10 cm apart and centered 7 cm above the vacuum slot. The sample was then inverted and passed through the deionized water spray a second time such that both sides of the web were sprayed with water. The deionized water spray was then removed, and the web was again passed over the vacuum slot to remove excess water. The web was then hung to dry at ambient conditions.

## EXAMPLE 11

A fluorinated poly-4-methyl-1-pentene meltblown microfiber web prepared according to Example 5 was charged following the procedure of Example 10.

## EXAMPLES 10A-11A

Examples 10A-11A were prepared following the procedures of Example 10 and 11 respectively, with the exception that, after corona fluorination and prior to hydrocharging, each of the fluorinated webs of Examples 10A-11A were subjected to an anneal at 140°C (300°F) for about 10 minutes.

## EXAMPLES 13, 15, 16, 18 and 20

Examples 13, 15, 16, 18 and 20 were charged following the procedure of Example 10, with the exception that the fluorinated polymeric fibrous webs used in each of Examples 13, 15, 16, 18 and 20 were as follows: a fluorinated polyethylene microfiber web prepared according to Example 3 above (Example 13); a fluorinated polyester staple fiber web prepared according to Example 4 (Example 15); a fluorinated G100 Filtrete fibrillated film web prepared according to Example 2 (Example 16); a fluorinated polypropylene needle punched web (12 denier/fiber fibers of Exxon 3505 polypropylene resin), having a basis weight of about 200 g/m<sup>2</sup>, and having been corona fluorinated following the method described in Example 1 (Example 18); and a polypropylene melt

blown fine fiber web, having a basis weight of  $46 \text{ g/m}^2$  and an effective fiber diameter of  $3.7 \text{ }\mu\text{m}$ , and having been corona fluorinated following the method described in Example 1 with the exception that 0.2%  $\text{C}_5\text{F}_{12}$  was used instead of 1%  $\text{C}_2\text{F}_6$  (Example 20).

5 DC Corona Charging

EXAMPLE 12

The fluorinated polyethylene meltblown microfiber web of Example 3 was charged using a DC corona discharge as follows. The fluorinated web was placed in contact with an aluminum ground plane, and then passed under an electrically positive DC corona source, in air, at a rate of about 1.2 meters/min, while maintaining a current to ground plane of about 0.01 mA/cm of corona source length. The distance from corona source to ground was about 4 cm.

EXAMPLES 14, 17, 19

15 Examples 14, 17 and 19 were charged following the procedure of Example 12, with the exception that the fluorinated polymeric fibrous webs for each of Examples 14, 17 and 19 were as follows: a fluorinated polyester staple fiber web prepared following the procedure of Example 4 (Example 14); a fluorinated polypropylene needle punched web (12 denier/fiber fibers made from Exxon 3505 polypropylene resin), having a basis weight of about  $200 \text{ g/m}^2$ , and having been corona fluorinated following the method described in Example 1 (Example 17); and a fluorinated polypropylene meltblown fine fiber web, having a basis weight of  $46 \text{ g/m}^2$  and an effective fiber diameter of  $3.7 \text{ }\mu\text{m}$ , and having been corona fluorinated following the method described in Example 1 with the exception that 0.2%  $\text{C}_5\text{F}_{12}$  was used instead of 1%  $\text{C}_2\text{F}_6$  (Example 19).

25

EXAMPLES 21-35

Examples 21-35 were prepared by fluorinating polypropylene blown microfiber webs following the procedure of Example 1, with the exception that the source of fluorine for each of Examples 21-35 was as follows: 1%  $\text{CF}_4$  (Examples 21-23), 1%  $\text{C}_2\text{F}_6$  (Examples 24-26), 0.1% hexafluoropropylene (Examples 27-29), 0.1%  $\text{C}_5\text{F}_{12}$  (Examples 30-32), and 1.0%  $\text{C}_5\text{F}_{12}$  (Examples 33-35).



The fluorinated webs of Examples 23, 26, 29, 32, and 35 were then charged following the hydrocharging process described above in Example 10.

The fluorinated webs of Examples 22, 25, 28, 31 and 34 were then charged following the DC corona charging process described above in Example 12.

- 5        % DOP penetration (“%DOP PEN”), Pressure Drop (mmH<sub>2</sub>O), and the Quality Factor (“QF”) for each of the electrets of Examples 10-35 were determined according to the above-described Initial DOP Penetration and Pressure Drop Test Procedure. The results are summarized in Table II.

10

TABLE II

EXAMPLE	% DOP PEN	PRESSURE DROP	QF
10	0.119	3.65	1.84
10A	0.140	3.21	2.05
11	2.45	1.46	2.54
11A	0.778	1.60	3.04
12	56.1	1.14	0.51
13	38.1	1.15	0.84
14	78.3	0.38	0.64
15	65.6	0.41	1.03
16	27.3	0.40	3.25
17	70.4	0.19	1.85
18	37.6	0.19	5.15
19	0.81	10.58	0.46
20	0.006	11.3	0.86
21	55.6	2.83	0.21
22	15.0	3.28	0.58
23	0.288	3.09	1.89
24	54.1	3.05	0.20
25	14.3	3.32	0.59
26	0.243	3.08	1.95
27	59.0	2.81	0.19
28	16.2	2.80	0.65
29	0.276	2.90	2.03
30	52.5	3.15	0.20
31	14.0	3.11	0.63
32	0.250	2.99	2.00
33	45.3	3.10	0.26
34	14.9	2.93	0.65
35	0.244	3.14	1.92

## EXAMPLES 36-39

Four fluorinated, polypropylene microfiber webs were prepared according to Example 1 with the exception that the source of fluorine containing species was as follows: 0.1% hexafluoropropylene ("HFP") (Examples 36 and 38) and 0.1% C<sub>3</sub>F<sub>12</sub> (Example 37 and 39).

Examples 36 and 37 further included charging the fluorinated polypropylene webs following the hydrocharging charging procedure of Example 10.

Examples 38 and 39 further included charging the fluorinated polypropylene webs following the DC corona charging procedure of Example 12.

Examples 36-39 were subjected to the above-described DOP Loading Test. The % DOP Penetration versus DOP loading (the amount of DOP collected on the web in grams) for each of Examples 36-39 was measured according to the above-described DOP Loading Test Procedure. The resulting data are plotted as % DOP penetration versus DOP load (grams) in Figs. 1 and 2 as follows: Examples 36 and 37 (indicated with x's and solid circles respectively) (Fig. 1), and Examples 38 and 39 (indicated with x's and solid circles respectively) (Fig. 2).

## EXAMPLE 40

A 7 in. by 7 in. sample of polypropylene microfiber web having a basis weight of 61 g/m<sup>2</sup> was placed under a nitrogen atmosphere. A gaseous mixture of 5% by volume elemental fluorine diluted in nitrogen was passed through the polypropylene microfiber web at a rate of 1.0 l/min for 10 minutes. The fluorine concentration was then increased to 10 % by volume diluted in nitrogen and passed through the web at a rate of 1.0 l/min for an additional 20 minutes.

The sample was then analyzed by ESCA and determined to have 62 atomic % fluorine and a CF<sub>3</sub>:CF<sub>2</sub> ratio of 0.59, as determined according to the above-described Method for Determining CF<sub>3</sub>:CF<sub>2</sub>.

The sample was then charged using a DC corona discharge as described above in Example 12, and subjected to the above-described DOP Loading Test. The resulting data are plotted as % DOP Penetration versus DOP Load (grams) in Fig. 3.

**EXAMPLE 41**

A polypropylene blown microfiber web, having a basis weight of 20 g/m<sup>2</sup> and a web width of 15 cm, was vacuum glow-discharge treated in a C<sub>5</sub>F<sub>12</sub> environment. The glow-discharge treatment was performed in a vacuum chamber. The vacuum chamber contained a roll-to-roll glow discharge system consisting of an unwind roller, glow discharge electrodes, and a windup roller for the continuous treatment of the blown microfiber web. Two stainless steel electrodes were in the parallel plate configuration, each electrode was 20 cm wide and 33 cm long and they were separated by a gap of 2.5 cm. The top electrode was grounded and the bottom electrode was powered by a 13.56 MHz rf generator (Plasma-Therm). The web traveled between the two electrodes and in contact with the top, grounded electrode so that one side of the web was exposed to the discharge.

After loading the roll of blown microfiber web onto the unwind roller under C<sub>5</sub>F<sub>12</sub> vapor at a pressure of 0.1 Torr. The blown microfiber web was advanced through the electrodes at a speed of 17 cm/min to achieve an exposure time to the plasma of 2 minutes. The discharge power was 50W. After the first side was treated, the chamber was vented and the web roll replaced onto the unwind roller to allow the other side of the web to be treated. The treatment of the second side of the web occurred under the same conditions as the first side. After the fluorination, Example 41 was DC-corona charged following the process described above in Example 12.

% DOP Penetration ("%DOP PEN") for Example 41 was determined according to the above-described Initial DOP Penetration and Pressure Drop Test Procedure. The results are summarized in Table III.

**TABLE III**

	% DOP Penetration
Loading Time (min)	Example 14
0.5	28
10	2°

Other embodiments are within the following claims. Although the electret has been described with reference to nonwoven polymeric fibrous webs, the electret can be a variety of polymeric articles including, e.g., those polymeric articles described in U.S. Patent Application Serial No. 09/106,506, entitled, "Structured Surface Filter Media,"  
5 (Insley et al.), filed on June 18, 1998 (attorney docket No. 53632USA2A).

All of the patents and patent applications cited above are incorporated by reference into this document in total.

## CLAIMS:

1. An electret comprising:  
a surface modified polymeric article having surface fluorination produced by  
5 fluorinating a polymeric article.
2. The electret of claim 1, wherein the surface modified polymeric article  
comprises at least about 45 atomic % fluorine as detected by ESCA.
- 10 3. The electret of claims 1-2, wherein the surface modified polymeric  
article comprises a  $\text{CF}_3:\text{CF}_2$  ratio of at least about 0.25 as determined according to the  
Method for Determining  $\text{CF}_3:\text{CF}_2$ .
- 15 4. The electret of claims 1-3, wherein the surface modified polymeric  
article comprises a  $\text{CF}_3:\text{CF}_2$  ratio of at least about 0.45 as determined according to the  
Method for Determining  $\text{CF}_3:\text{CF}_2$ .
- 20 5. The electret of claims 1-4, wherein the surface modified polymeric  
article has a Quality Factor of at least about 0.25/mmH<sub>2</sub>O.
6. The electret of claims 1-5, wherein the surface modified polymeric  
article has a Quality Factor of at least about 0.5/mmH<sub>2</sub>O.
- 25 7. The electret of claims 1-6, wherein the surface modified polymeric  
article has a Quality Factor of at least about 1/mmH<sub>2</sub>O.
8. The electret of claims 1-7, wherein the surface modified polymeric  
article comprises a nonwoven polymeric fibrous web.

9. The electret of claims 1-8, wherein the surface modified polymeric article comprises a nonwoven polymeric fibrous web comprising fibers selected from the group consisting of polycarbonate, polyolefin, polyester, halogenated polyvinyl, polystyrene, or a combination thereof.

5

10. The electret of claims 1-9, wherein the fibrous web comprises fibers selected from the group consisting of polypropylene, poly-(4-methyl-1-pentene), or a combination thereof.

10

11. The electret of claims 1-10, wherein the surface modified polymeric article comprises meltblown microfibers.

15

12. An electret comprising a polymeric article comprising at least about 45 atomic % fluorine as detected by ESCA and a having  $\text{CF}_3:\text{CF}_2$  ratio of at least about 0.45 as determined according to the Method for Determining  $\text{CF}_3:\text{CF}_2$ .

13. The electret of claim 12, wherein the article has a  $\text{CF}_3:\text{CF}_2$  ratio of greater than 0.9.

20

14. The electret of claims 12-13, wherein the article has a Quality Factor of at least about  $1/\text{mmH}_2\text{O}$ .

25

15. The electret of claims 12-14, wherein the article comprises a nonwoven polymeric fibrous web that comprises fibers that contain polypropylene, poly-(4-methyl-1-pentene), or a combination thereof.

30

16. The electret of claim 15, wherein the fibers are melt-blown microfibers that have an effective fiber diameter of less than 50 micrometers, preferably 3 to 30 micrometers, and more preferably 7 to 15 micrometers.

17. An electret comprising a polymeric article comprising at least about 50 atomic % fluorine as detected by ESCA and a  $\text{CF}_3:\text{CF}_2$  ratio of at least about 0.25 as determined according to the Method for Determining  $\text{CF}_3:\text{CF}_2$ .

5 18. The electret of claims 17, wherein the polymeric article comprises a  $\text{CF}_3:\text{CF}_2$  ratio of at least about 0.45, preferably a  $\text{CF}_3:\text{CF}_2$  ratio of greater than about 0.9, as determined according to the Method for Determining  $\text{CF}_3:\text{CF}_2$ .

10 19. The electret of claims 17-18, wherein the polymeric article has a Quality Factor of at least about 0.5/mmH<sub>2</sub>O.

20. The electret of claims 23-26, wherein the fibrous web comprises melt-blown microfibers that contain polypropylene, poly-(4-methyl-1-pentene), or a combination thereof.

15 21. An electret that comprises:  
a nonwoven web that comprises polymeric microfibers, the web has surface fluorination that comprises  $\text{CF}_3$  and  $\text{CF}_2$  at a  $\text{CF}_3:\text{CF}_2$  ratio of at least 0.45 as determined according to the Method for Determining  $\text{CF}_3:\text{CF}_2$ .

20 22. The electret of claim 21, which possesses a Quality Factor of at least about 1.0 per mm H<sub>2</sub>O.

25 23. The electret of claims 21-22, wherein the article has a surface fluorination of at least about 45 atomic % fluorine as detected by ESCA.

24. The electret of claims 21-23, wherein the  $\text{CF}_3:\text{CF}_2$  ratio is at least 0.9.

30 25. The electret of claims 21-24, wherein the microfibers are melt-blown microfibers that have an effective fiber diameter of 1 to 50  $\mu\text{m}$ .

26. The electret of claims 21-35, wherein the microfibers are melt-blown microfibers that have an effective fiber diameter of 3 to 30  $\mu\text{m}$ , preferably 7 to 15  $\mu\text{m}$ .

5 27. The electret of claims 21-26, wherein the microfibers are made from a resin that has a resistivity less than  $10^{14}$  ohm-cm.

28. The electret of claims 21-27, wherein the microfibers comprise polyolefin.

10 29. The electret of claims 21-28, wherein the microfibers comprise polypropylene.

30. The electret of claims 21-29, wherein the nonwoven web has a basis weight of 10 to 100  $\text{g/m}^2$ .

15

31. The electret of claims 21-30, wherein the nonwoven web has a thickness of 0.25 to 20 mm.

20 32. The electret of claims 21-31, wherein the microfibers have been fluorinated by transferring a fluorine containing species from a gaseous phase to the nonwoven web.

25 33. The electret claim of claim 21-32, wherein the microfibers have been fluorinated by exposing the nonwoven web to an atmosphere that includes a fluorine containing species.

34. The electret of claim 33, wherein the atmosphere is a controlled atmosphere.

30 35. The electret of claim 34, wherein the controlled atmosphere is free of oxygen.



36. The electret of claims 33-35, wherein the fluorine containing species includes fluorine atoms, elemental fluorine, or fluorocarbons.

5 37. The electret of claims 21-36, wherein the microfibers have been electrically charged through a DC corona discharge process.

38. A method of making an electret, comprising:  
fluorinating a polymeric article to produce an article having surface  
fluorination; and  
10 charging the fluorinated article in a manner sufficient to produce an electret.

39. The method of claim 38, wherein the polymeric article is a nonwoven web that contains microfibers that have an effective fiber diameter of 1 to 50 micrometers.

15 40. The method of claims 38-39, comprising charging the fluorinated article by contacting the fluorinated article with water in a manner sufficient to produce an electret, and drying the article.

20 41. The method of claims 38-40 comprising charging the fluorinated article by impinging jets of water or a stream of water droplets onto the fluorinated article at a pressure and for a period sufficient to produce an electret, and drying the article.

25 42. The method of claims 38-40, comprising fluorinating a polymeric article in the presence of an electrical discharge to produce a fluorinated article.

43. The method of claims 38-41, comprising fluorinating the polymeric article in the presence of an alternating current corona discharge at atmospheric pressure.

30 44. The method of claims 38-42, comprising fluorinating the polymeric article in an atmosphere comprising fluorine containing species selected from the group consisting of elemental fluorine, fluorocarbons, hydrofluorocarbons, fluorinated sulfur, fluorinated nitrogen or a combination thereof.

45. The method of claim 43, wherein the fluorine containing species are selected from the group consisting of  $C_5F_{12}$ ,  $C_2F_6$ ,  $CF_4$ , hexafluoropropylene,  $SF_6$ ,  $NF_3$ , or a combination thereof.

5

46. The method of claim 43, comprising fluorinating the polymeric article in an atmosphere comprising elemental fluorine.

47. The method of claim 39, wherein the electret comprises  $CF_3$  and  $CF_2$  groups on the surface of the fibers at a  $CF_3:CF_2$  ratio of at least about 0.45 as determined according to the Method for Determining  $CF_3:CF_2$ .

10

48. The method of claims 38-47, comprising charging the fluorinated article with a direct current corona discharge to produce an electret.

15

49. The method of claim 48, further comprising annealing the fluorinated article prior to charging the fluorinated article.

50. A filter comprising the electret of claims 1-49.

20

51. A respirator comprising the filter of claim 50.

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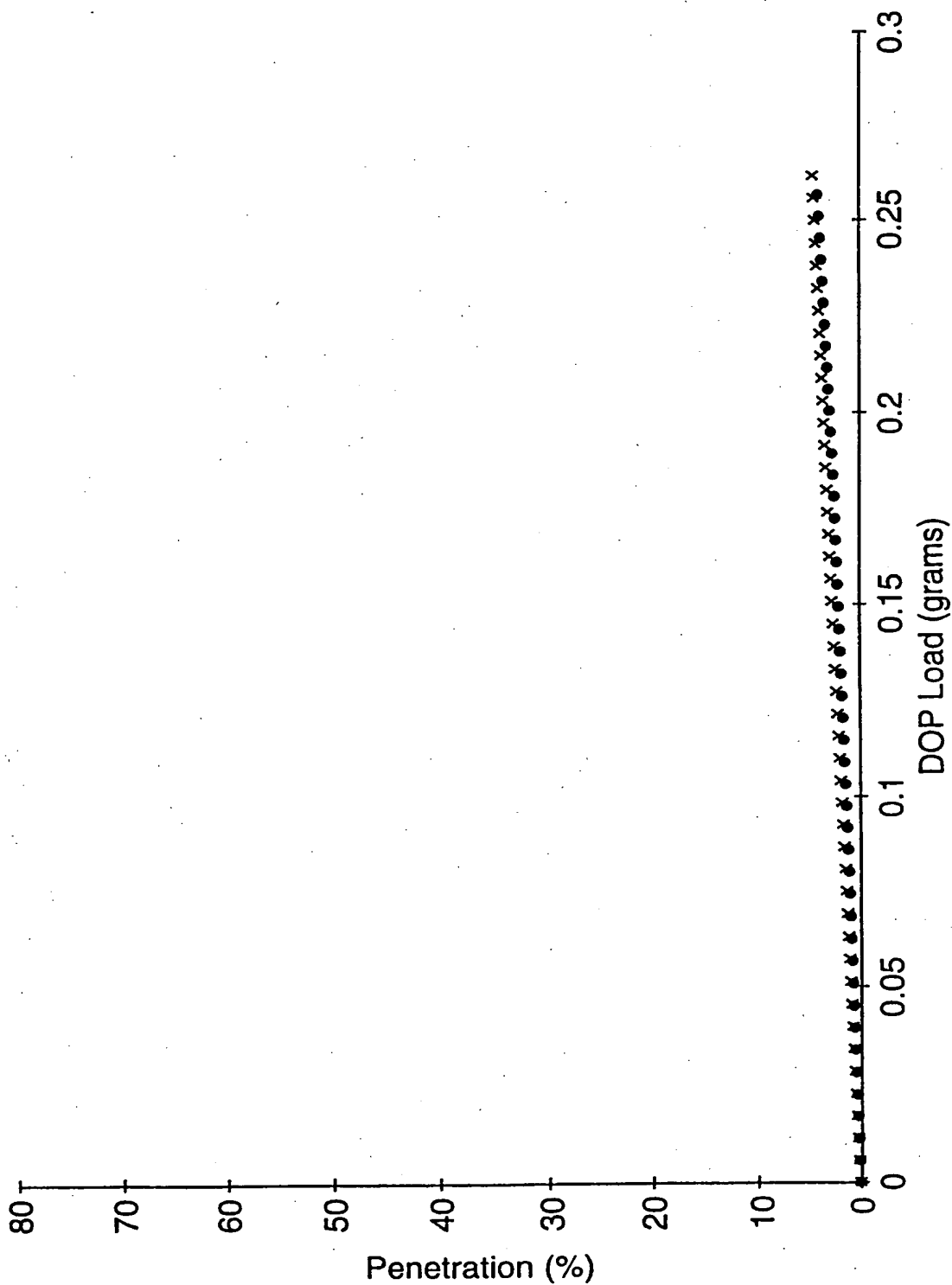


Fig. 1

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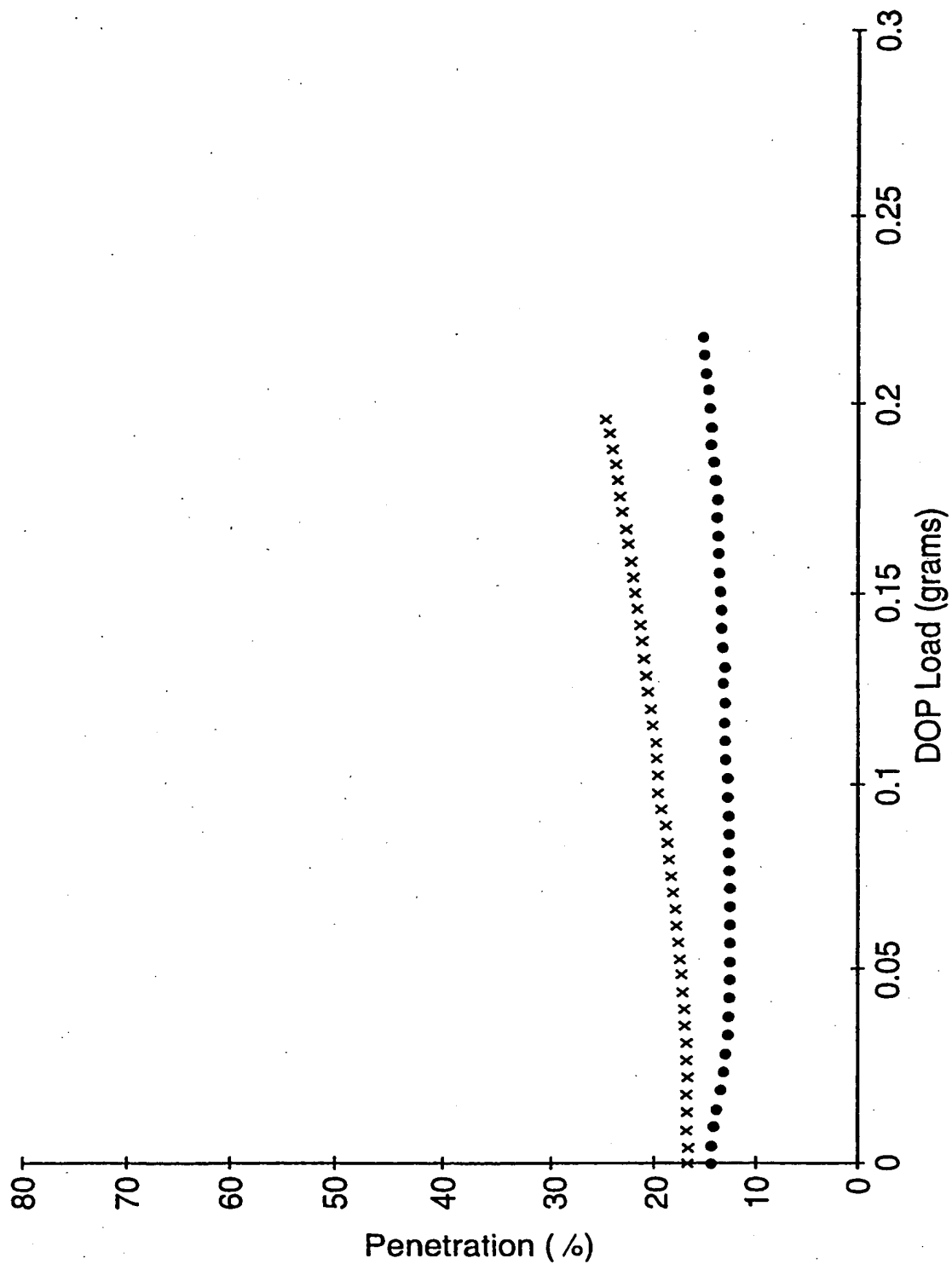
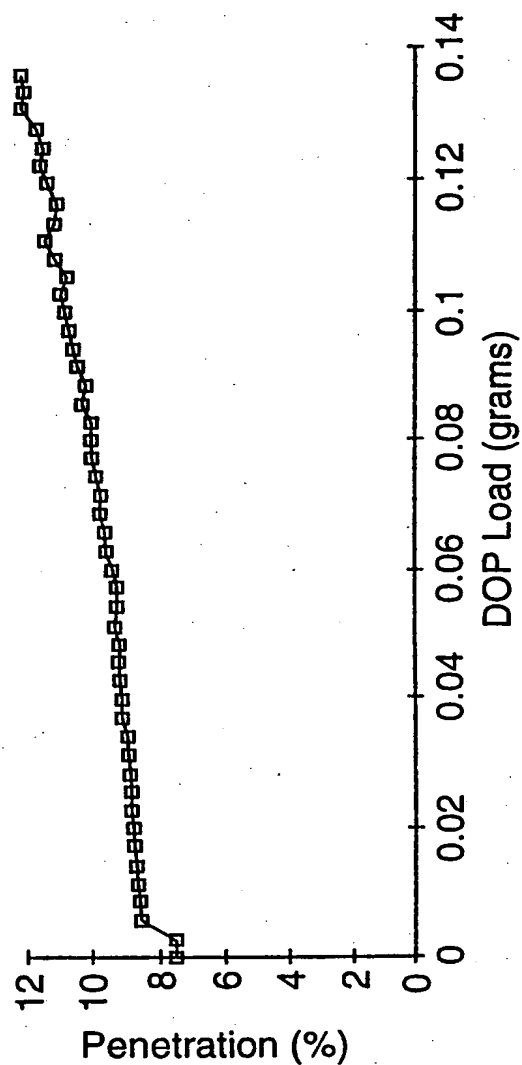


Fig. 2

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**Fig. 3**

# INTERNATIONAL SEARCH REPORT

International Application No

PC 99/13917

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C08F/24 B03C3/28

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C08F B03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 850 692 A (KOKEN LTD.) 1 July 1998 (1998-07-01) page 3, line 2 - line 3 page 4, line 26 - line 37 ---	1-4, 8, 50, 51
X	US 5 110 620 A (TANI, Y. ET AL.) 5 May 1992 (1992-05-05) column 4, line 28 - line 42 ---	1-4
Y	DATABASE WPI Section Ch, Week 199619 Derwent Publications Ltd., London, GB; Class A88, AN 1996-182763 XP002900714 & JP 08 057225 A (SEKISUI CHEM IND CO LTD) , 5 March 1996 (1996-03-05) abstract --- -/--	1-50

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

22 November 1999

Date of mailing of the international search report

17. 12. 1999

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# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 99/13917

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	<p>DATABASE WPI Section Ch, Week 199344 Derwent Publications Ltd., London, GB; Class A85, AN 1993-347672 XP002900715 &amp; JP 05 253416 A (MITSUI PETROCHEM IND CO LTD), 5 October 1993 (1993-10-05) abstract</p>	1-50
A	<p>GB 2 060 259 A (NEDERLANDSE ORGANISATIE VOOR TOEGEPAST-NATUURWETENSCHAPPELIJK) 29 April 1981 (1981-04-29)</p>	1-50
A	<p>EP 0 616 831 A (MINNESOTA MINUNG AND MANUFACTURING CO.) 28 September 1994 (1994-09-28)</p>	1-51
A	<p>US 4 188 426 A (AUERBACH, R.A.) 12 February 1980 (1980-02-12)</p>	1-49

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PC1, 99/13917

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 850692	A	01-07-1998	JP 10180021 A	07-07-1998
			US 5935303 A	10-08-1999
-----				
US 5110620	A	05-05-1992	JP 1258714 A	16-10-1989
			JP 2536584 B	18-09-1996
			JP 1199614 A	11-08-1989
			JP 2595586 B	02-04-1997
			DE 3839956 A	08-06-1989
			US 5112677 A	12-05-1992
-----				
JP 8057225	A	05-03-1996	NONE	
-----				
JP 5253416	A	05-10-1993	NONE	
-----				
GB 2060259	A	29-04-1981	NL 7907539 A	14-04-1981
			DE 3038381 A	23-04-1981
			FR 2467474 A	17-04-1981
			JP 56100409 A	12-08-1981
			SE 452525 B	30-11-1987
			SE 8007120 A	12-04-1981
-----				
EP 616831	A	28-09-1994	AU 669420 B	06-06-1996
			AU 5756894 A	29-09-1994
			BR 9401208 A	08-11-1994
			CA 2116983 A	27-09-1994
			DE 69419272 D	05-08-1999
			JP 6319923 A	22-11-1994
			US 5411576 A	02-05-1995
			US 5472481 A	05-12-1995
-----				
US 4188426	A	12-02-1980	NONE	
-----				